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RUTILE TITANIUM DIOXIDE AND ITS USE IN POLYMER SYSTEMS

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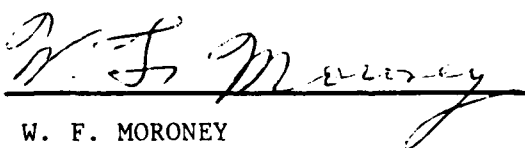
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Titanium dioxide is extensively used as a filler in polymer systems because of its ability to impart whiteness, opacity, and chemical stability to the resulting composite. The manufacturing process, properties of rutile titanium dioxide are reviewed. The properties of composites produced from titanium dioxide and polymer systems are also reviewed. These properties are discussed in relation to polymer-particle interactions. An approach is presented to study polymer-pigment interactions by analyzing thermodynamic properties such as enthalpy, entropy, and free energy of adsorption. *Keywords: polymer chemistry; coatings; (K?)*

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TABLES

FIGURES

INTRODUCTION

World consumption of titanium dioxide in 1987 was approximately 2.5 million tons, primarily being used in the paint, paper, plastic, and rubber industries as a particulate filler. It is the most important single pigment used in paints due to its physical and chemical properties which enable it to provide chemical stability, high reflectance, brightness, and opacity. TiO_2 exists in three crystal structures: rutile, anatase, and brookite. Figure 1 illustrates the rutile and anatase structures. Although anatase has been used in polymer systems, rutile is by far the most commonly used form due to the instability of the other two forms and, because of its relative importance, rutile will be the subject of this report.

Table 1 lists properties of rutile titanium dioxide. TiO_2's stability is exemplified by its relative inertness up to its melting point of 1830°C and its insolubility in all liquids except concentrated sulfuric and hydrofluoric acids at elevated temperature. This exceptional chemical stability is attributed to the strong bond between the titanium ion, which is tetravalent, and the bivalent oxygen ion, resulting in the physical shielding of titanium ions by six oxygen ions (1). The brightness and opacity which rutile characteristically imparts to polymer systems are due to its reflection of nearly all visible light, high refractive index and optimum particle size. Figure 2 illustrates the reflectance of rutile TiO_2 through the near ultraviolet, visible, and infrared wavelengths. The whiteness of this material is obvious from its nearly 100% reflectance throughout the visible region. The slight absorption in the 400 - 425 micron wavelengths results in a bluesh tone to some grades of TiO_2.

For white particulate dispersed composites, opacity is caused by pigment scattering light, preventing it from reaching the substrate. In this case, light scattering is primarily dependent upon index of refraction and this relationship can be expressed by the Lorentz-Lorenz equation (2):

$$M = \frac{(n_p/n_b)^2 - 1}{(n_p/n_b)^2 + 2} \tag{1}$$

where: M = Lorentz-Lorenz expression
n_p = refractive index of the pigment
n_b = refractive index of the continuous phase

Opacity has been shown to be directly proportional to M^2 (3), thus an increase in the n_p/n_b ratio will increase opacity. Titanium dioxide has one
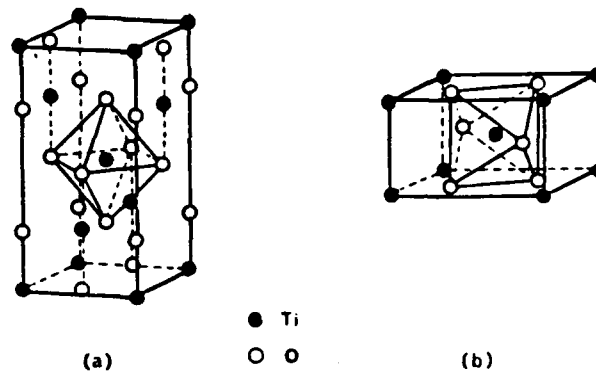
FIGURE 1:   TITANIUM DIOXIDE CRYSTAL STRUCTURES.
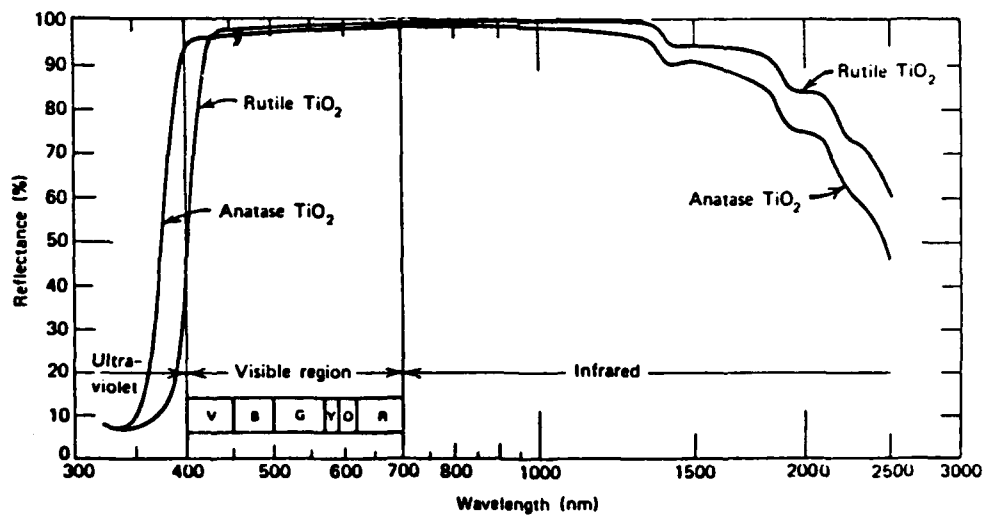(a) ANATASE. (b) RUTILE. (2)

FIGURE 2:   REFLECTANCE SPECTRA OF TITANIUM DIOXIDE (1).

of the highest refractive indices of white pigments (Table 2) and therefore it is the optimum white pigment to obtain opacity. Table 2 also lists M^2 for the pigment in a binder with a refractive index of 1.5. Note the significant effect in the magnitude of M^2 with a change in the index of refraction of the pigment.

TABLE 1: TYPICAL PROPERTIES OF RUTILE TITANIUM DIOXIDE (1).

Appearance	White powder
Density (g/cm^3)	4.24
Surface area (m^2/g)	9-25
Refractive index	2.76
Oil absorption (g oil/100g pigment)	16-48
Tinting strength (Reynolds)	1650-1900
Particle size, avg. (microns)	0.2-0.3
Hardness (moh)	6-7
Melting point ($^{\circ}$C)	1830
Specific heat (cal/$^{\circ}$C-g)	0.17
Dielectric constant	114
Entropy @ 298.16°K (cal/deg-m)	12.01 (2)

TABLE 2: INDEX OF REFRACTION FOR COMMON WHITE PIGMENTS (4) AND THE LORENTZ-LORENZ EXPRESSION

	REFRACTIVE INDEX	M^2
Titanium dioxide	2.61	0.163
Zinc oxide	2.01	0.044
Zinc sulfate	2.37	0.111
Lithopone	1.84	0.021
Antimony oxide	2.04	0.049
Zirconium oxide	2.15	0.068
Silica	1.54	0.0003

Another important property affecting opacity is particle size. An empirical relationship for the optimum particle size for light scattering by white pigments is (3):

$$d_{opt} = \frac{\lambda}{4.44 n_b M} \qquad (2)$$

where λ is the wavelength of light considered. For rutile titanium dioxide in an acrylic binder, d_{opt} is 0.19 microns at a wavelength of 560 nm (green light). For this reason, titanium dioxide is specifically manufactured with particle diameters ranging from 0.18 to 0.25 nm. The combined effects of negligible visible light absorption, high refractive index, and tailored particle size distribution enable TiO_2 to impart significantly more whiteness and hiding power to polymer systems than any other common pigment. For this reason, along with its ability to be manufactured relatively inexpensively,

rutile's use is widespread.

One deficiency of titanium dioxide is its susceptibility to lose small amounts of oxygen upon exposure to radiant energy. Since titanium dioxide is a strong absorber of ultraviolet light (Figure 2), this degradation process is prominent when exposed to these wavelengths. The process occurs when electrons are excited from the valence band to the conduction band, also causing positive holes in the valence band. The conduction band electrons and the positive holes are free to move about the lattice. The positive holes which reach the surface of the pigment can react with hydroxyl groups, forming hydroxyl radicals. The free electrons react with adsorbed oxygen to form O_2^- ions. In addition, the oxygen ions can react with water to form $HO_2 \cdot$. These reactions are illustrated below (5):

$$Positive\ hole + OH^- \quad \text{--------->} \quad OH \cdot$$

$$Electron + O_2 \quad \text{------------->} \quad O_2^-$$

$$O_2^- + H_2O^- \quad \text{----------------->} \quad OH^- + HO_2 \cdot$$
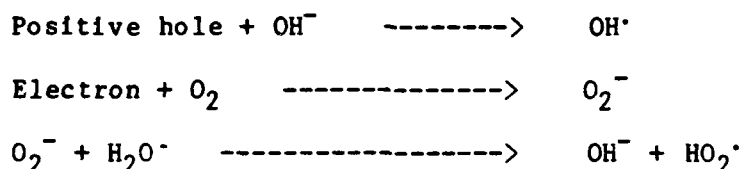
When a composite material consisting of titanium dioxide dispersed in a polymer system is exposed to UV radiation, the free radicals and ions formed from the photochemical degradation of the TiO_2 are likely to react with the surrounding polymer, especially if this polymer is also susceptible to oxidation and/or UV degradation. Figure 3 illustrates this process which is described as chalking when occuring with paints. Fortunately, the surface of titanium dioxide is amenable to modification with organic and inorganic treatments that alleviate this problem. These treatments will be described briefly later in this report. It is interesting to note that although chalking is usually undesirable because it indicates a breakdown of the coating, in some paints it is specifically desired. For example, some exterior house paints are designed to chalking because the continuous exposure of fresh pigments provides a long lasting clean appearance. Table 3 summarizes specific applications of titanium dioxide in coatings, plastics, textiles, and other commercial products.

TABLE 3: USE OF TITANIUM DIOXIDE IN COMMERCIAL PRODUCTS (1).

| END PRODUCT	REASONS FOR USE
COATINGS AND PAINTS	To opacify the medium in which it is dispersed. To impart brightness, whiteness, and gloss control. Also, to improve durability of paints, especially exterior coatings.
PLASTICS	To impart brightness and whiteness, improve strength and durability.
TEXTILES	To de-luster synthetic fibers to reduce gloss of fabrics.
PAPER	To obtain opacity and improve brightness.
CERAMICS	To provide ultraviolet screening for containers, especially those manufactured for food storage.

PIGMENT

INCREASING
EXPOSURE
TIME
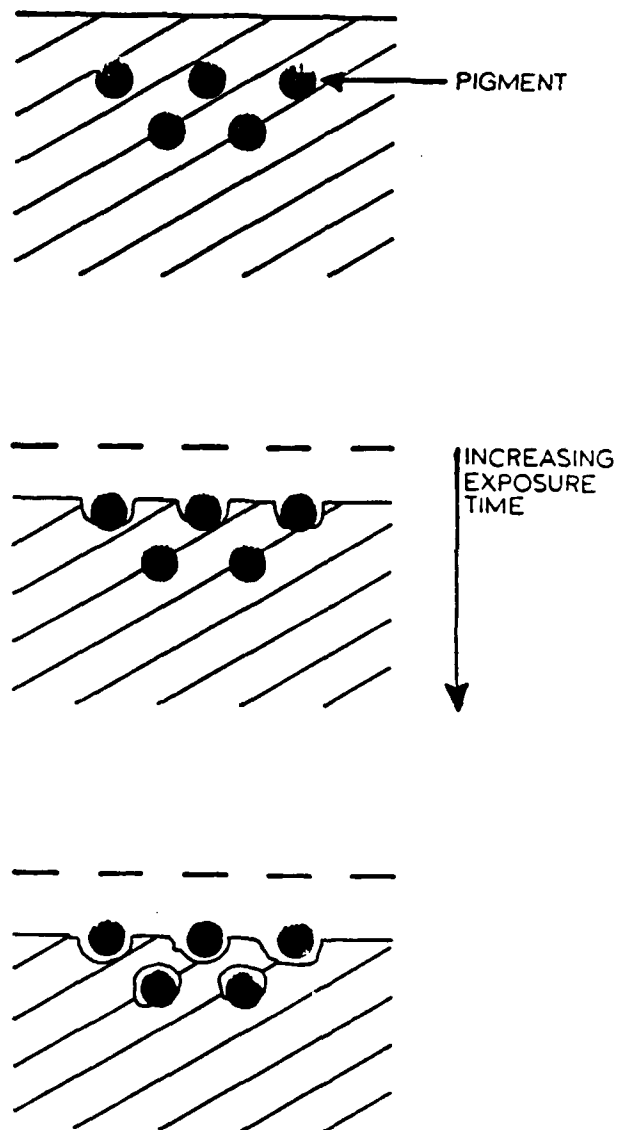
FIGURE 3: SCHEMATIC ILLUSTRATION OF PHOTOCATALYTIC DEGRADATION
OF A PAINT FILM.

MANUFACTURING AND COMMERCIAL GRADES

Although the general manufacturing processes for titanium dioxide have been followed for years and are well understood, there are many processing details which are proprietary. This is especially true of the surface treatments which improve the compatibility and durability of rutile in polymer systems. There are several methods to manufacture TiO_2; however, hydrolysis in aqueous solutions, the "sulfate process", is the most common commercial approach. This process initiates with the drying and grinding (200 mesh) of ilmenite ore, $FeTiO_3$. Afterward, the ore is dissolved in concentrated sulfuric acid to form iron and titanium sulfates. These sulfate salts are subsequently dissolved further in sulfuric acid. Metallic iron is added to reduce the ferric salts to the ferrous state. Undissolved salts and impurities are removed with the use of a coagulant, causing this sediment to settle. The mixture is filtered and the solution is concentrated by evaporation of water. Upon cooling, any ferrous sulfate remaining is precipitated by cooling the solution.

The titanium sulfate solution is heated, and titania "seeds" (extemely small crystals) are introduced to initiate the hydrolysis of titanium salts. Hydrous titanium dioxide is precipitated, filtered and washed. In order to obtain rutile, "promoters" are added which preferentially yield the rutile crystal structure. The material is then calcined in rotary kilns in order to dehydrate the material and initiate crystallization. Special treatments can be added at this stage to modify the material. The product is ground to the desired primary pigment size and the final "pretreatments" are applied to the surface, depending on the desired end use.

Surface modifications are applied to titanium dioxide to improve color stability, chalk resistance, ease of dispersion, and hiding power. These treatments can be inorganic and/or organic surface layers. Common inorganic treatments are zinc oxide, alumina, silica, and antimony oxide. For example, TiO_2 coated with alumina is known to have improved color stability which reduces a tendency of certain paints to yellow under various light conditions (6,7,8). Table 4 lists several grades of inorganic surface treated rutile. Although organic treatments are used to improve pigment-polymer compatibility which in turn improves dispersion properties, these treatments are proprietary. Examples of some potential organic treatments are polyhydric alcohol, an alkanolamine, and silicone oils.

Due to the various uses of titanium dioxide, there are over 100 commercially available grades. These grades mainly vary in particle size and surface treatment. Reference (9) provides a detailed list of the common commercially available grades of titanium dioxide.

SURFACE CHARACTERISTICS

A gallon of house paint may contain up to 2 pounds of titanium dioxide, having a total surface area of nearly 3.5 acres. Because of this magnitude of exposed pigment surface area, the dispersion and durability properties of polymer formulations containing titanium dioxide are significantly influenced by the pigment's surface characteristics. Surface charge, energy, and acidity along with interparticle forces determine the potential pigment-polymer

interactions which may occur. Interparticle forces are primarily Van der Waals and London attractions which are formed when particles approach each other at distances on the order of several angstroms. These forces are responsible for agglomeration of dry particles. Surface charge on pigment particles is present in the form of an electrical double layer. When a pigment is emersed in any liquid media, an electrophoretic potential is created by ions adsorbing on the surface in a different concentration than that in the solution. The type of ions, size and concentration determine the charge scheme and magnitude of the double layer. Surface energy is present due to the different interatomic relationships between particles on the surface versus those in the bulk of the pigment. This surface energy is not only a characteristic of the material but also defines how this material will interact with other materials, specifically its wetting properties when immersed in a liquid. Titanium dioxide is amphoteric, potentially exhibiting basi^ or acidic surface properties depending on its actual surface treatment and the medium in which it is dispersed. Although these surface characteristic control the performance of titanium dioxide pigments in polymer systems, it is difficult to provide specific characteristics for the general class of titanium dioxide because the different grades of these pigments are coated with different proprietary treatments (10,11). However, it is important to strictly characterize the specific pigment being used when investigating pigment-polymer interactions.

TABLE 4: TYPICAL SURFACE TREATED GRADES OF RUTILE TITANIUM DIOXIDE (6).
(APPROXIMATE COMPOSTIONS, PERCENT BY WEIGHT)

DESIGNATION	TiO_2	ZnO	Al_2O_3	SiO_2	SPECIAL PROPERTIES
OR-250*	98	---	---	--	General purpose type
OR-342	97	---	1.0	--	Color retention in enamels
OR-540	95	---	2.0	0.75	Chalk resistance, interior use
OR-640	94	1.0	2.1	0.80	High chalk resistance, exterior use

*Manufactured by American Cyanamide Company

An example of the potential activity of the titanium dioxide surface is seen with its interaction with water. Anhydrous titanium dioxide readily adsorbs water onto its entire surface. The thickness of this adsorbed water layer has been found to be 2 monolayers thick at $21^{\circ}C$ and relative humidities of 60-70%. The extent and strength of the interaction with water can vary. This is exemplified by attempts to remove the adsorbed water layer. Loosely bound, physically adsorbed water can be removed at temperatures below $120^{\circ}C$. Physically adsorbed water which is more tightly bound can be removed by heating above $120^{\circ}C$. Finally, chemisorbed water which is bound to the TiO_2 surface by hydrogen bonds is removed by heat to $300^{\circ}C$, however even at $450^{\circ}C$, isolated hydroxyl groups remain on the surface (10,11). This attraction of water to titanium dioxide illustrates the large surface interactions which are possible between titanium dioxide and adsorbing species.

INTERACTIONS WITH POLYMERS

Although particulate fillers have significant effects on the mechanical and physical properties of polymer systems, relatively little research has been done with regard the mechanical effects of titanium dioxide. A wealth of information is readily available on this subject for silica and carbon black fillers but, even though titanium dioxide is a commonly used pigment, research regarding its effects on mechanical properties is lacking. One reason for this may be the numerous grades of titanium dioxide, all having different surface treatments. Another reason may be that although titanium dioxide is used extensively in paints, its use is not driven by mechanical properties and therefore paint researchers are not as concerned with these effects. Fortunately, the fact that TiO_2 surface variations exist and are common allows for conventient study of their effects.

Boluk and Schreiber (12) have studied the dynamic mechanical responses of chlorinated polyethylene (CPE) when formulated with various grades of titanium dioxide. None of the rutile grades effected the T_g of the CPE polymer. This result is slightly unexpected since studies with other polymer-filler materials have reported two glass transitions (13). The "second" glass transition in these composites is due to the different state of the polymer in the adsorption layer versus that in the bulk phase. The adsorbed material is "bound" and less mobile than it would normally be in an unattached state as in the bulk phase and it is responsible for the additional, slightly higher, T_g. One explanation for this effect not being observed with titanium dioxide in CPE may be the low specific surface area of titanium dioxide pigments (9 to 25 m^2/g) versus other fillers such as silicas and carbon blacks which are normally in the 200 to 300 m^2/g range. Having a lower surface area theoretically should result in less adsorbed polymer and thus less potential for a second phase and a second T_g.

Reference (12) also reports that the damping peak of CPE was depressed by addition of titanium dioxide and that the magnitude of this effect varied for different grades of TiO_2. These results were analyzed using two theories. The first is a model by Iisaka and Shibayama (14) relating damping of particulate filled composites to the pure matrix polymer:

$$TAN \ \delta_c = T \delta_p (1 - B_\delta)$$

(3)

where p and c refer to the pure polymer and composite, respectively. δ is the volume fraction of filler, and B is the polymer adsorbed layer thickness on the pigment. The second theory is the acid-base interaction parameter introduced by Drago (15) and recently popularized by Fowkes (16,17). In general, the acid-base interaction theory states that an electron accepter (Lewis acid) will strongly interact with an electron donor (Lewis base). A parameter is used to relate relative acid-base nature. Negative interaction parameters indicate acidic tendencies and positive parameters indicate basic tendencies. The data from the current study indicated there is an obvious trend that the more basic pigments had a greater damping effect than acidic particles. In addition, variations in CPE adsorbed layer thickness (as calculated using equation (3)) were found for the different pigment grades. Figure 4 illustrates that the more basic titanium dioxide grades result in

increase adsorbed layer thicknesses. These results are expected because CPE is acidic due to its chlorine groups which are capable of strong interactions with the basic pigments. The effect is observed for pigment acid-base parameters up to approximately 1.5, above which, increased alkalinity of the pigment has little effect. Although the acid-base parameter for CPE was not provided, it is possible that a stoichiometric limitation exists on the polymer-pigment (acid-base) interaction. Finally, although modulus characteristics were analyzed with different grades of TiO_2, no relationship with pigment-particle interactions were found. It should be noted that titanium dioxide with silica dominant surface treatments tend to be acidic while those with alumina treatments tend to be basic (18).

As stated above, there is relatively little information on the mechanical effects of TiO_2 on polymer systems. However, the above information certainly indicates that it does have influence on mechanical properties. Although the acid-base interaction theory has been successfully used to predict polymer-pigment interactions, thermodynamic data such as enthalpy, entropy, and free energy may provide a clearer picture of these interactions. Use of this information would eliminate the need for assumptions about polymer adhesion onto filler materials, including fibers. These assumptions are common in the development of models for mechanical properties. Therefore, it is likely that improvement in these models would result from accurate thermodynamic polymer-pigment interaction data. A summary of several recent studies concerning adsorption of organic species onto titanium dioxide is provided below.

Stieg's review of titanium dioxide surface characteristics (19) provides several fundamental yet important issues concerning adsorption. Table 5 lists the heat of submergence or wetting of TiO_2 in several liquids. This data indicates that the heat of adsorption increases with adsorbate polarity and, theoretically, more polar interactions are stronger and more stable. In addition, other results show that a trace of polar impurities in nonpolar solvents raises the heat of wetting to nearly that of pure polar substance. For example, the data in Table 5 illustrates that adding 0.02% water to benzene raises the heat of submergence from 0.390 cal/g for pure benzene to 0.805 cal/g, which is 89% of that for pure water. The amount of impurity required to observe this effect is just enough to form a monolayer on the pigment surface. This suggests that the primary interaction of adsorbate molecules in direct contact with the adsorbent is strong and dominent, and that subsequent interactions are shielded from the actual pigment surface by the adsorbed layer. Stieg states this is the case, especially when an adsorbate molecule has both polar and non-polar characteristics. For example, oleic acid has an acid group at one end of the molecule, extending from a large aliphatic chain. Upon adsorption of oleic acid onto TiO_2, the polar acid group will bond to the surface while the aliphatic chain will extend perpendicular from the surface. Interestingly, the resulting "particle" appears to have a relatively nonpolar surface. Finally, the author makes considerable note that although much research is performed on titanium dioxide, in reality the surface of the pigment is usually not TiO_2 but rather some inorganic or organic treatment and this must be characterized and · considered when interpreting results.
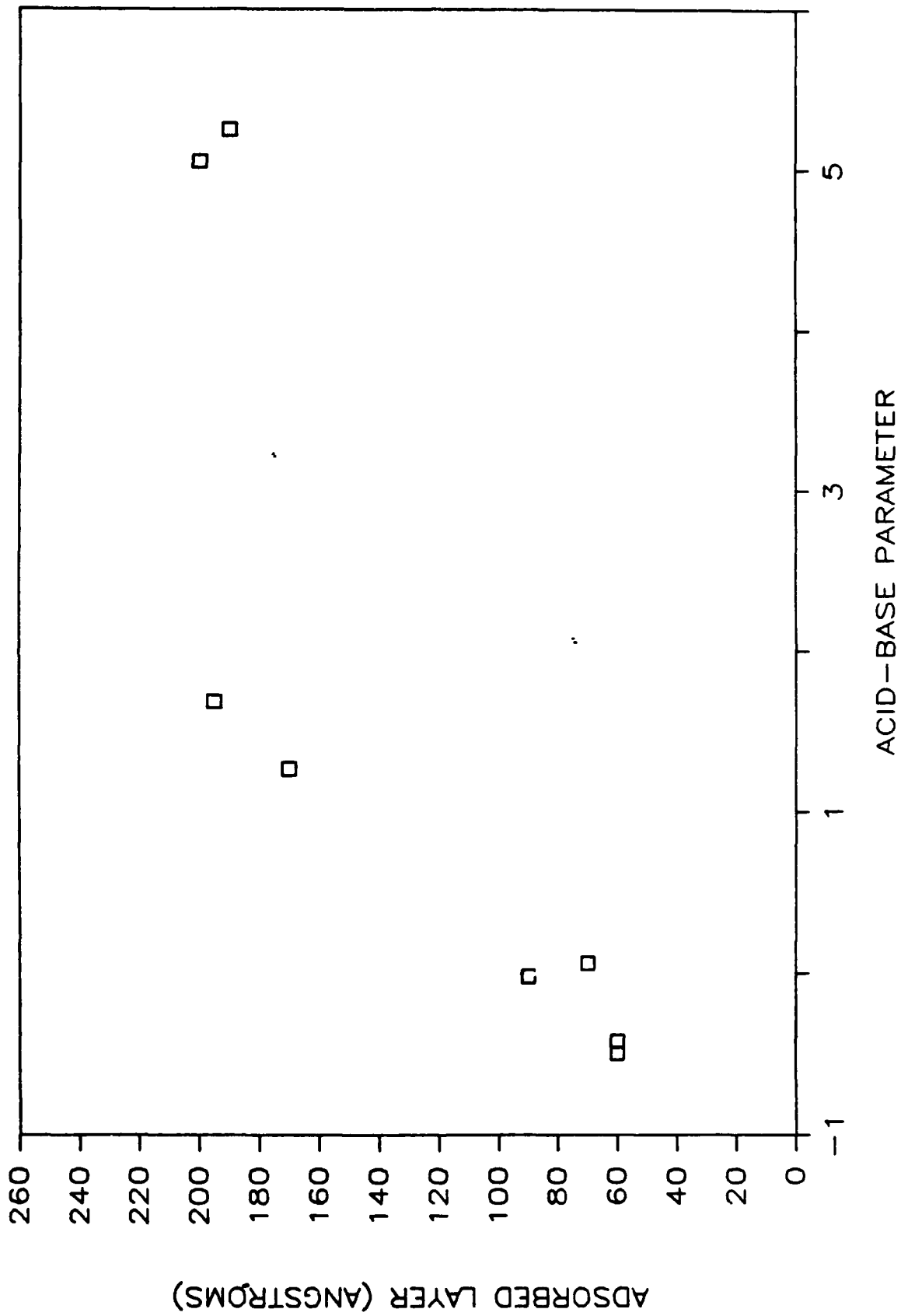
FIGURE 4: ADSORBED LAYER THICKNESSES OF CPE ON TITANIUM DIOXIDE PIGMENTS WITH VARIOUS ACID-BASE INTERACTION PARAMETERS (19).

TABLE 5: HEAT OF SUBMERGENCE OF TiO_2 IN VARIOUS COMPOUNDS (19).

Water	1.15 CAL/G
Butyric acid	0.883
Ethyl acetate	0.800
Butyl alcohol	0.796
Carbon tetrachloride	0.526
Benzene	0.390
0.01% H_2O in benzene	0.805
0.02% H_2O in benzene	1.024

Many of the generalities about adsorption onto titanium dioxide discussed by Stieg are experimentally confirmed by Suda and Nagao (20). By studying the adsorption of n-BuOH, n-BuCl, and $n-C_7H_{16}$ onto titanium dioxide, they found that the affinity for TiO_2 increased from the alkane, to the chloride, to the alcohol. Furthermore, the alcohol tends to orient perpendicular to the surface while the other adsorbates lie parallel or flat on the surface. This is due to the strong hydrogen bond which is formed between the pigment surface and the hydroxyl group within the alcohol. The n-BuCl and $n-C_6H_{16}$ form weaker dipole and Van der Waals bonds. Interestingly, the results indicated that the number of irreversibly adsorbed molecules decreased linearly with increasing surface hydroxyl content. Although adsorption onto these hydroxyl groups can occur, a stronger chemisorption can occur if they can be replace by the adsorbing species.

Day and Egerton (21) also studied the adsorption of alcohols onto titanium dioxide. Ethanol adsorption was attributed to both hydrogen bonding and a chemical reaction with surface hydroxyl groups. The strength of adsorption was significantly greater in the latter due to the primary bonds which are suspected. It is assumed that most alcohols would undergo similar adsorption unless steric hinderances or competing preferential adsorption by other groups or compounds are factors. It was also found that although compounds containing a single hydroxyl orient perpendicular to the surface, multi-hydroxyl compounds tend to lie flat and adsorb at multiple sites. This effect should be considered if tailoring the adsorption layer is desired since the strength of the adsorption should be at least linearly increasing with the functionality of the adsorbing species.

SUMMARY

Titanium dioxide is extensively used as a filler in polymer systems because of its ability to impart whiteness, opacity, and chemical stability. One deficiency of untreated titanium dioxide is its susceptibility to degradation by radiant energy. In order to alleviate this problem and to improve dispersion properties, most grades of TiO_2 are surface treated with inorganic or organic coatings.

The primary method of processing titanium dioxide is the sulfate process by reducing and removing the ferric salts from the raw ore $FeTiO_3$. The resulting titanium dioxide particles are specifically manufactured with diameters ranging from 0.18 to 0.25 microns for optimum opacity. The surface is also modified with one or several treatments depending on the intended use

of the pigment. These surface treatments can be inorganic (alumina, silica, zinc oxide) and/or organic (polyhydric alcohol, amines, silicones).

Because the main reasons for using titanium dioxide are optical properties and chemical stability, their is little data available on mechanical and physical effects of TiO_2 in polymer systems. However, various grades of rutile titanium dioxide were found to have no effect on the T_g of chlorinated polyethylene but certain grades did depress the damping peak. This influence was attributed to the interaction of the basic pigment surface with the acidic polymer. These effects were far less apparent with acidic grades of titanium dioxide.

Heats of submergence and adsorption of species onto titanium dioxide increase with increasing polarity of the species. The concentration of the adsorbing species need only be sufficient to form a monolyer on the pigment surface. The orientation of the adsorbed compound depends on its chemical structure. Linear compounds with both a polar and nonpolar end will tend to orient perpendicular to the surface, with the polar group adsorbing onto the surface. Nonpolar molecules tend to lie flat on the surface however they are easily removed by stronger adsorbing species. Finally, compounds with multiple polar sites can orient parallel to the surface, adsorbing at several sites and their removal is difficult because of the strong adsorption behavior.

It is interesting to note that many of the adsorption characteristics described for titanium dioxide have been observed on other surfaces, especially silica. The affinity of various types of organic species, adsorption strength, and adsorbate molecular orientations are similar. There are two obvious reasons for these similarities. The first reason is that in many cases the surface of the titanium dioxide particle is all or partially silica. The second is that many pigments have surface hydroxyl groups and which are subsequently hydrated and, as such, these different pigments exhibit similar surface characteristics.

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